

Thermodynamic Analysis of Hydrogen Production from Methanol Reforming in Supercritical Water

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Keywords: Hydrogen; Methanol; Reforming; Thermodynamic Analysis; Supercritical Water.

Abstract. The hydrogen production via methanol reforming in supercritical water (SCW) condition has been thermodynamically investigated by a Gibbs free energy minimization method to determine equilibrium yields and energy requirements in fuel processor over the temperature range between 673 and 1273 K and water-to-methanol (H₂O:MeOH) ratio of 1 – 5 corresponding to the methanol concentration from 64 to 26 wt%, respectively. In this research, the main objective is to compare the influence of operating pressure from atmospheric (ATM) pressure to SCW condition on the product yields. At ATM pressure, a hydrogen production increases with increasing reaction temperature up to 973 K while under SCW condition, an increase of temperature constantly increases the formation of hydrogen. As the reaction temperature increases, the hydrogen production and the total heat load increase but the hydrogen to carbon monoxide (H₂/CO) ratio decreases. Although the hydrogen yield is constantly higher at ATM pressure than under SCW condition, the H₂/CO ratios are always greater in SCW at temperatures above approximately 700 K. The amount of hydrogen and the heat load of both the preheater and the reactor also increase significantly as the H₂O:MeOH ratio increases.

Introduction

As the growing demand of hydrogen fuel for fuel cell application is expected in the near future, the efficient production of hydrogen is very important enabling technology for commercialization of fuel cell for both of residence and automobile. Normally, hydrogen can be produced under atmospheric or near atmospheric pressure, such as steam reforming, autothermal reforming and partial oxidation. As the expense of high-pressure compressed hydrogen tank is too high, the development of a very high-pressure process for the direct production of hydrogen is attractive to avoid high cost of hydrogen storage [1]. The reaction in supercritical water (SCW) provides many advantages over the conventional technologies because of the special physical characteristics of SCW [2]. Above the critical temperature and pressure ($T_c \geq 647$ K, $P_c \geq 22.1$ MPa), the properties of water such as ion product, density, dielectric constant, and viscosity are immensely different from those of the normal liquid or steam at atmospheric (ATM) pressure [3, 4].

A number of researchers have studied the production of hydrogen in supercritical water from a variety of primary sources, such as methanol [1, 5, 6], ethanol [7, 8] and biomass [9]. Among a variety of fuel sources, methanol is a good raw material for hydrogen production because of the high hydrogen to carbon ratio and the absence of carbon-carbon bonds [5]. Moreover, methanol is easy to store and transport as it is liquid phase at normal conditions.

The study into thermodynamic model is very useful to provide theoretical guidance for optimizing operating conditions. There are several works on thermodynamic analysis of methanol reforming [10-12]. Voll et al. [13] conducted thermodynamic analysis of supercritical water gasification of methanol at operating conditions 973 K and 27.6 MPa, and different feed concentrations of methanol between 15 and 45 wt% and different reaction temperatures between 823 and 973 K by using the Gibbs free energy minimization. There has been little research work done on thermodynamic analysis

of hydrogen production via methanol reforming in supercritical water. The present study aims to investigate the effect of operating conditions on the product contribution. The chemical equilibrium analysis is determined by the Gibbs free energy minimization. A previous work on thermodynamic analysis of methanol reforming and oxidation in SCW was investigated by Srisiriwat and Wutthithanyawat [14]. However, there have been no thermodynamic studies on methanol reforming for pressures ranging from ATM pressure to SCW conditions. The use of SCW would be particularly suited for the production of high pressure H_2 from liquid fuels. If a high pressure purification system can be developed, then significant reduction in compression duty could be achieved if the hydrogen has to be stored in high-pressure reservoirs. In this study, a thermodynamic analysis of hydrogen production from methanol reforming at various temperatures and amount of water in the reactant feed at reactor pressures ranging from ATM to SCW conditions is investigated. The amount of H_2 , CO , CO_2 and CH_4 yields are reported as well.

Methodology

The process diagram of a hydrogen production from methanol reforming is shown in Fig. 1. The mixed methanol and water are fed to the preheater before entering the reformer to produce the hydrogen-rich gas using as fuel in a fuel cell.

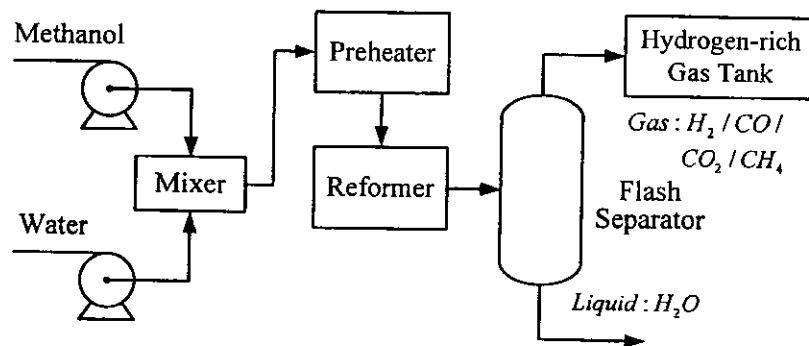


Figure 1 Schematic diagram of hydrogen production from methanol reforming.

Thermodynamic analysis is an important part of hydrogen production researches because it can be used to make a decision for choosing the suitable conditions and it gives fundamental information since the equilibrium conversion will be always the best one. In this study, a thermodynamic equilibrium prediction using a Gibbs free energy minimization can be performed to determine the product composition at which the Gibbs free energy of the products is at a minimum when a multi-component system reaches chemical equilibrium [14]. An equation of state has been chosen to describe the thermodynamic behavior of each species in the SCW system. Peng-Robinson equation of state [15] is adopted for the phase equilibrium calculations in supercritical fluids, which is a complex system with properties far from those of conventional fluids [16] because Peng-Robinson equation of state has been widely used in the field of supercritical fluids. The yield of all product species i can be calculated with the equations below:

$$Y_i = \frac{F_{i,out}}{(F_{MeOH,in} - F_{MeOH,out})} \quad (1)$$

where $F_{i,in}$ and $F_{i,out}$ represent the molar flowrate (mol/sec) of species i measured at the inlet and outlet of the reformer, respectively. $F_{MeOH,in}$ is based on 1 mol/sec of methanol fed to the SCW reactor.

Results and Discussion

For fixed steam-to-methanol ($\text{H}_2\text{O}:\text{MeOH}$) ratio of 1, the effects of reaction temperature, ranging between 673 and 1273 K, on gas yields of H_2 , CO , CO_2 and CH_4 at ATM pressure and SCW condition are shown in Figs. 2(a) and 2(b), respectively. In all investigated conditions, methanol conversion was more than 99.9%. The major gas products observed were H_2 , CH_4 , CO_2 and CO . Theoretically, a steam reforming of methanol offers the highest obtainable hydrogen yield of 3 in the product gas as presented in Eq. (2)



In fact, the stoichiometric coefficient of H_2 is less than 3 because in the methanol reforming other methanol reactions can take place simultaneously, such as, dehydration, decomposition, and dehydrogenation [11].

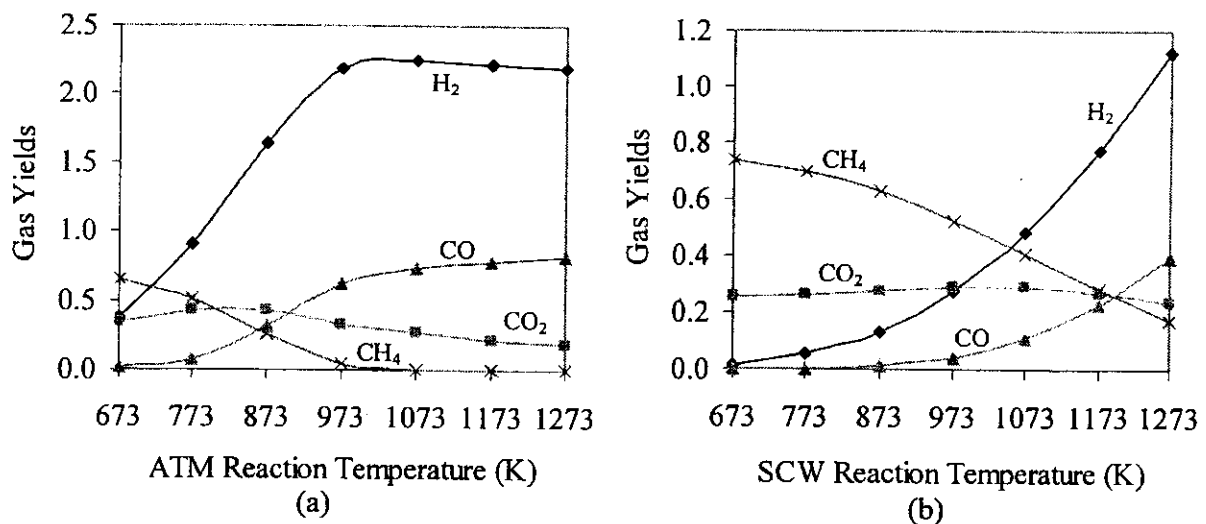


Figure 2 Effect of reaction temperature on gas yields at $\text{H}_2\text{O}:\text{MeOH}$ ratio of 1 at pressure (a) 0.1 MPa (ATM) and (b) 25 MPa (SCW).

Although the thermodynamic analysis approach of the minimization of Gibbs free energy, in which the possible chemical equation is not necessary, was applied in this paper, the reactions involved in the production of hydrogen by the reforming of methanol can be used to describe the occurrence of product distribution. The major reactions [5, 13, 17] involved in the reforming of methanol are following:

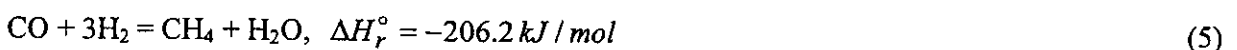
Methanol decomposition:



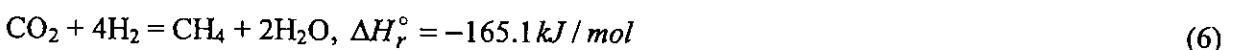
Water-gas shift reaction:



Methanation of CO:



Methanation of CO_2 :



The reaction temperature has a significant effect on the product distribution. An increase of reaction temperature causes an increase of amount of H_2 and CO whereas a CH_4 and CO_2 formation decreases. At ATM pressure, CH_4 is completely converted at temperature above 973 K; in contrast, under SCW conditions, CH_4 also appears in the system though the reaction temperature is greater than

1273 K resulting in the lower H_2 production compared with a result at ATM pressure. Although the hydrogen yield is constantly higher at ATM pressure than under SCW condition, the values of H_2/CO ratio are always greater in SCW at temperature above approximately 700 K as illustrated in Fig. 3(a) for constant $H_2O:MeOH$ ratio of 1. Moreover, the total heat load in the system is always higher at ATM pressure than under SCW conditions as shown in Fig. 3(b). Under SCW condition, an increase of H_2 production is because higher conversion at higher temperatures which indicate the endothermic nature of the methanol decomposition (Eq. (3)) [5]. Furthermore, a decrease of CH_4 formation caused an increase of H_2 and CO compositions because of the occurrence of methane reforming reaction which is the reverse reaction in Eq. (5). However, it should be noticed that the small amount of CO was obtained.

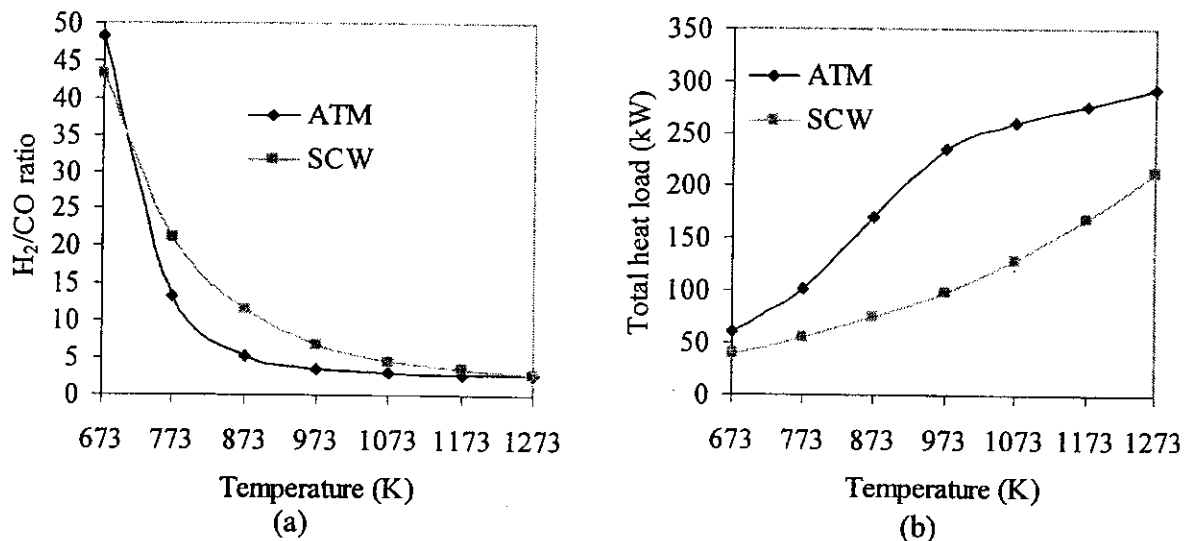


Figure 3 Effect of reaction temperature on (a) H_2/CO ratio and (b) total heat load.

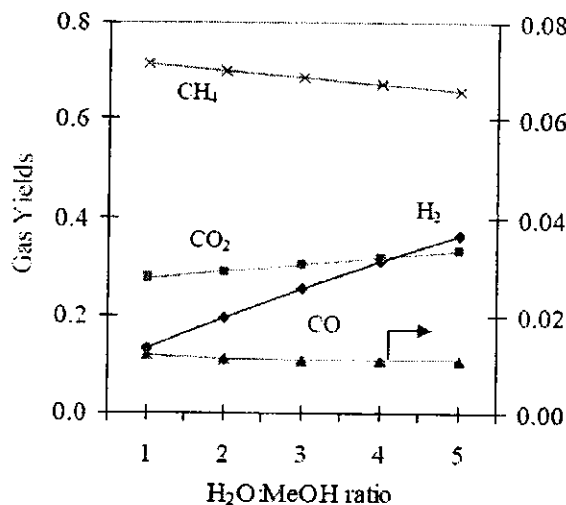


Figure 4 Effect of $H_2O:MeOH$ ratio on product yields at reaction temperature of 873 K.

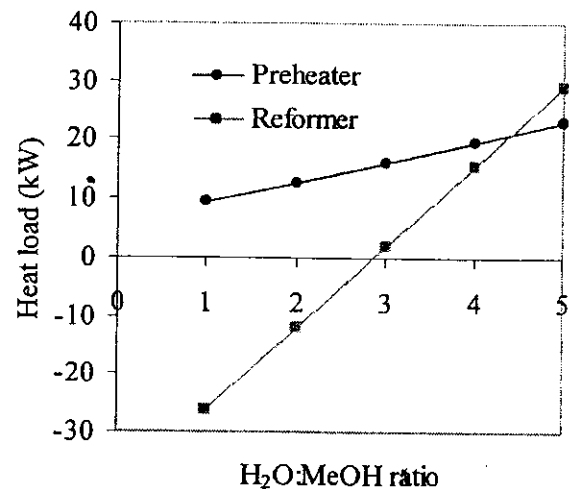


Figure 5 Effect of $H_2O:MeOH$ ratio on heat load of preheater and reformer at reaction temperature of 873 K.

Fig. 4 shows the effect of $H_2O:MeOH$ ratio, ranging between 1 and 5 corresponding to the methanol concentration from 64 to 26 wt%, respectively, on the product yields at fixed reaction temperature of 873 K. It can be found that, an increase in the $H_2O:MeOH$ ratio (or a decrease in methanol concentration) causes an increase of amount of H_2 and CO_2 . Concurrently, the CO_2 content increases according to water-gas shift reaction in Eq. (4). The methanation reaction (Eq. (6)) is

avored at high feed concentration (low H₂O:MeOH ratio) but, when the H₂O:MeOH ratio is higher, the equilibrium of this reaction is shifted backward, leading to a decrease in the CH₄ yield.

The results in this study were compared with the work of Tang and Kitagawa [18], who performed thermodynamic analysis with direct Gibbs free energy minimization for supercritical water gasification of biomass including methanol. The tendency of product distribution showed good agreement with the numerical results of thermodynamic model proposed by Tang and Kitagawa [18].

Fig. 5 illustrates the effect of H₂O:MeOH ratio on the heat load of preheater and reformer at fixed reaction temperature of 873 K. Although an increase of H₂O:MeOH ratio can improve the H₂ yield, the energy requirement for driving the fuel processor, including preheater and reformer also increases. At below H₂O:MeOH ratio of 3, the heat load of reformer appears in the negative range that means, the exothermic reaction occurs so the cooling medium is provided for maintaining the reaction temperature.

Conclusion

From a thermodynamic point of view, the product distribution and energy requirement during methanol reforming was investigated for a wide range of pressure from ATM to SCW conditions. The effects of temperatures between 673 and 1273 K and H₂O:MeOH ratios between 1 and 5 on product yields and heat load were reported. The reaction temperature has a very important effect on the product yield and the total heat load of fuel processor. Although hydrogen formation is always better at ATM pressure than under SCW conditions, the H₂/CO ratio is consistently higher under SCW condition at temperature roughly 700 K due to the significantly lower amount of CO produced. In this work, it can be concluded that the hydrogen production from methanol reforming in SCW is favored at the high temperature and amount of water in feed although the higher heat load supplying for fuel processor is required.

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